Shining APS light on nanoscale oxidation

Scientific Achievement

Using a new environmental chamber at the Advanced Photon Source (APS), we discovered that the early-stage oxidation behavior of the copper (001) surface differs in many important aspects from expectations based on macroscopic theory and previous ex-situ, later-stage experimental studies. Using our ability to monitor oxide growth at temperature, in-situ, we find that the critical oxygen partial pressure delineating the thermodynamic limit between oxide growth and reduction is more than nine orders-of-magnitude larger for thin-film samples than predicted by bulk phase equilibria. Substrate-induced strain in the copper and the nanometer-scale size of the initial oxide islands are believed responsible for this behavior. The results were reported in *Applied Physics Letters* (vol. **87**, 051914, 2005). We also observe large reversible changes in the oxide lattice parameter, up to 0.5%, in response to controlled variations in oxygen partial pressure in the chamber. Such behavior suggests that the oxygen stoichiometric range of Cu_2O nano-islands is much larger than previously reported for the bulk oxide. Additionally, we see important differences in the oxidation behavior of thin film versus bulk samples. Single crystal Cu_2O islands that nucleate and grow on substrate-constrained (001) Cu thin films at 350°C remain perfectly crystallographically-aligned with the metal as the oxide islands grow. In contrast, the Cu_2O islands that grow on bulk single crystal samples at the same temperature and oxygen partial pressure, while nucleating exactly aligned with the metal lattice, undergo a distinct tilting transformation as the oxide grows. Differences in strain states between thin film and bulk samples are believed responsible for this behavior.

Significance

Despite the enormous economic importance of metal oxidation, our knowledge of the underlying mechanistic processes involved is extremely limited. In particular, a substantial gap exists between the information available from surface-science studies, *i.e.*, at low oxygen coverage, and that provided by bulk oxidation studies. This knowledge-gap is being bridged at the APS in unprecedented detail via in-situ x-ray characterization of growing oxide films. By revealing the importance of strain and oxide island size at early stages of oxide coverage, this study has identified key phenomena that must be understood in order to realize the overarching goal of obtaining a predictive, atomic-level understanding of oxidation. This study also demonstrates the value of developing advanced instrumentation for in-situ observations in controlled environments. The insight that is arising through these studies will prove valuable in considerations of oxidation remediation design strategies.

Performers

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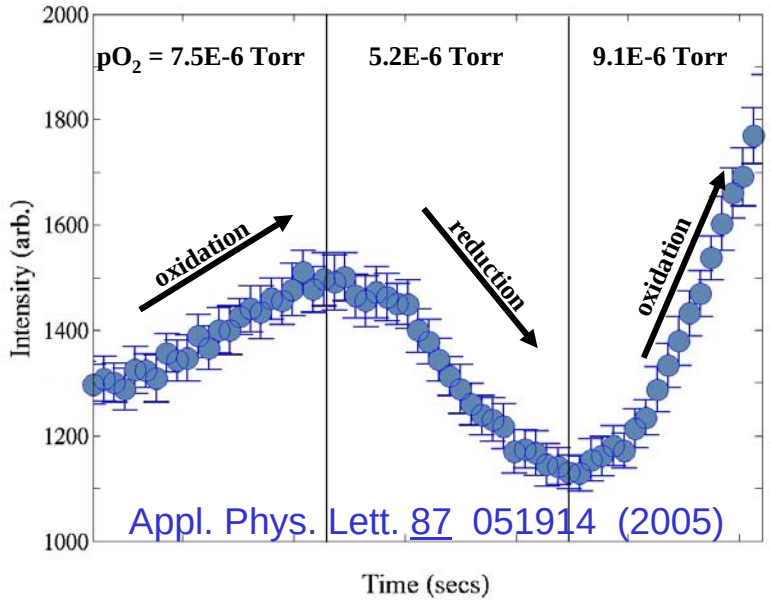
Strain and oxide nano-island size have a surprising effect on early-stage copper oxidation.

In-situ oxidation chamber (BESSRC Sector 12, APS)



Cu_2O Bragg peak intensity during oxidation and reduction at 450°C in controlled pO_2

- The pO_2 boundary between oxidation and reduction of oxide nano-islands on Cu thin films is >9 orders-of-magnitude higher than predicted by bulk thermodynamics.
- In-situ capabilities at APS are key to obtaining insight into early-stage oxidation behavior.
- Future studies using this approach will impact our understanding of catalysis, hydrogen storage, etc.

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